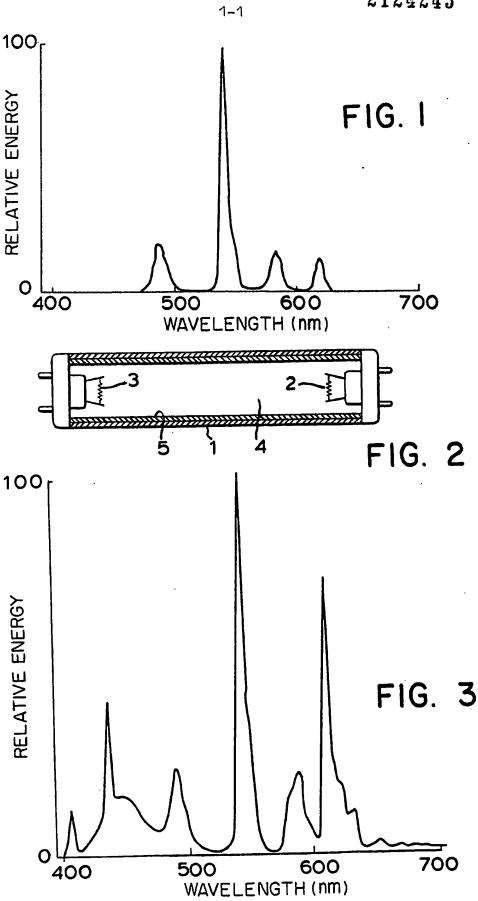
# UK Patent Application (19) GB (11) 2 124 243 A

- (21) Application No 8320036
- (22) Date of filing 26 Jul 1983
- (30) Priority data
- (31) 57/129876
- (32) 26 Jul 1982
- (33) Japan (JP)
- (43) Application published 15 Feb 1984
- (51) INT CL<sup>3</sup> C09K 11/467 11/463 11/475
- (52) Domestic classification C4S 311 43Y 703 705 709 711 715 719 737 739 749 75Y 755 757 758 76Y 764 765 771 78Y H1D 12B47Y 12B4 35 5G 9A 9Y U1S 1925 C4S H1D
- (56) Documents cited GBA 2112800 GB 1232612 GB 1214257 GB 1134798
- (58) Field of search C4S
- (71) Applicant Mitsubishi Denki Kabushiki Kaisha (Japan), 2—3 Marunouchi 2chome, Chiyoda-ku, Tokyo, Japan
- (72) Inventor
  Katsuo Murakami,
  Saburo Umeda,
  Hitoshi Yamazaki
  Norihiko Tanakr.
  Hiroshi Ito
- (74) Agent and/or Address for Service Marks and Clerk, 57—60 Lincoln's Inn Fields, London WC2A 3LS

- (54) A green-emitting phosphor and a low pressure mercury vapor lamp employing this phosphor
- (57) A green-emitting phosphor for a low pressure mercury vapor discharge lamp has a monoclinic monazite-type crystal structure and comprises a phosphate of cerium, terbium, and possibly lanthanum, yttrium, gadolinium or lutetium. It is significantly different from green-emitting phosphors of the prior art in that it further comprises at least one element selected from the alkali metals, fluorine, indium, and boron. Because of the addition of these

elements, the decrease in powder brightness of the present phosphor after heating in air at 600°C (the temperature at which phosphors are heated during the baking step of lamp manufacture) is much less than for conventional green-emitting phosphors. The decrease in brightness of the present phosphor after irradiation by ultraviolet light at 185 nm is also much less than for conventional phosphors. It is accordingly most appropriate for use in discharge lamps. The low pressure mercury vapor discharge lamp using the present phosphor is of high efficiency and has excellent colour rendering.





10

35

40

55

## **SPECIFICATION**

A green-emitting phosphor and a low pressure mercury vapor lamp employing this phosphor

#### BACKGROUND OF THE INVENTION

The present invention relates to a novel type of green-emitting phosphor, and also to low pressure mercury vapor discharge lamps using this type of phosphor. Green-emitting phosphors using terbium (Tb) as an activator have many practical applications, being widely used in low pressure mercury vapor discharge lamps, high pressure mercury vapor discharge lamps, cathode-ray tubes, and other devices. For example, Japanese Patent Publication No. 48—22117 discloses a mixture of blue, green, and redorange-emitting phosphors of relatively narrow spectral distribution for use in a 3-band fluorescent lamp. Also, Japanese Patent Laid Open No. 50—61887 discloses a green-emitting fluorescent lamp for copy machines.

A number of terbium-activated phosphors exist in the prior art. Terbium-activated cerium orthophosphate phosphors [(Ce, Tb) PO<sub>4</sub>] were introduced in "The Journal of Chemical Physics" (Volume 51, 1969 No. 8, p. 3252). Also, terbium-activated lanthanum cerium orthophosphate phosphors [(Cew, La, Tb)PO<sub>4</sub>] were disclosed in Japanese Patent Laid Open No. 54—56086. The cerium (Ce) in these phosphors absorbs ultraviolet radiation. The absorbed energy is transmitted to terbium, and green light is emitted by terbium, the emission spectrum of which has a peak in the vicinity of 545 nm.

However, when these orthophosphate phosphors are used in mercury vapor discharge lamps the
resulting lamps have emission outputs far lower than would be expected based on the power brightness of the phosphors. As a result of experiments upon which the present invention is based, it became clear that there are 2 main causes for low emission output by orthophosphate phosphor mercury vapor discharge lamps. One is that heating in air causes the cerium in the phosphors to become easily oxidized (changing from a valency of 3 to a valency of 4), and therefore, at the time of lamp manufacture, heating during the backing step produces a significant decrease in brightness. The other cause for low emission output is that in low pressure mercury vapor lamps, irradiation by ultraviolet light at 185 nm produced by the discharge causes a decrease in brightness in an extremely short time.

## SUMMARY OF THE INVENTION

The object of the present invention is to solve the above-described problems of the prior art and provide a phosphor which suffers but little deterioration in its qualities during the baking step and which 30 exhibits only a small decrease in brightness when used in mercury vapor discharge lamps.

It is a further object of the present invention to provide a low pressure mercury vapor lamp using this phosphor which has a high emission output combined with high efficiency and high color rendition.

These and other objects of the present invention will become clear upon reading the following description and upon studying the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the emission spectrum of a phosphor according to the present invention as set forth in Example 8.

Figure 2 is a cross-sectional view of one embodiment of a low pressure mercury vapor lamp using 40 a phosphor according to the present invention.

Figure 3 shows the spectral distribution of the emission from a fluorescent lamp employing a phosphor according to the present invention as set forth in Example 45.

# DESCRIPTION OF THE PREFERRED EMBODIMENTS

The phosphor according to the present invention comprises a phosphate of the Group III B

45 elements cerium and terbium, or of cerium, terbium, and at least one other element of Group III B of the Periodic Table selected from the group consisting of lanthanum, yttrium, gadalinium, and lutetium, and further comprises at least one element selected from the alkali metals, fluorine, indium, and boron. This phosphor is further characterized by having a monoclinic monazite-type crystal structure. A low pressure mercury vapor discharge lamp according to the present invention is characterized in that either all or part of the phosphor layers in the lamp are composed of this phosphor. A low pressure mercury vapor lamp according to the present invention has one or more phosphor layers, each of which includes a red-orange-emitting phosphor and the above-described phosphor according to the present invention or a red-orange-emitting phosphor, the phosphor according to the present invention, and a blue-emitting phosphor.

The above described, well-known terbium-activated cerium orthophosphate phosphor and the terbium-activated lanthanum cerium orthophosphate phosphor both possess monoclinic monazite -type crystal structures. The phosphor according to the present invention possesses this same type of crystal structure. Also, like the phosphors of the prior art, the phosphor according to the present invention is a phosphate comprising cerium, terbium, and possibly lanthanum. However, it is essentially different from the prior art phosphors in that it contains at least one element selected from the alkali metals, fluorine, inclum, and boron.

25

30

The introduction of these elements minimizes the decrease in brightness due to heating, decreases the reduction in brightness resulting from irradiation with ultraviolet light at 185 nm, and increases the powder brightness. Accordingly, the phosphor according to the present invention is extremely appropriate for use in mercury vapor discharge lamps. This phosphor can be excited no only by ultraviolet light but also by electrons, and thus can be used in cathode-ray tubes and similar devices.

Hereinafter, a number of examples of phosphors according to the present invention will be described in order to show the effects of changes in composition on the characteristics of the phosphor as well as to show the preferred composition of the phosphor.

## **EXAMPLE 1**

Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), cerium nitrate [Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O], and terbium oxide (Tb<sub>4</sub>O<sub>7</sub>) were dissolved in nitric acid to prepare a 10 I solution containing 0.65 gram atoms of lanthanum, 0.15 gram atoms of cerium, and 0.20 gram atoms of terbium. This solution was gradually added dropwise into a 10 I solution containing 2.4 moles of oxalic acid and reaction was carried out at approximately 80°C. The resulting precipitate of oxalate was filtered and dried. This oxalate was heated at 1000°C—1100°C for approximately 1 hour to change it into an oxide. The oxide was then thoroughly mixed with 0.90 moles of diammonium hydrogen phosphate [(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>] and 0.10 moles of boric acid (H<sub>3</sub>BO<sub>3</sub>) and then baked at 1200°C for 1 hour in a reducing atmosphere (nitrogen containing 5% hydrogen). The baked product wa pulverized and then sieved to obtain a phosphor.

The composition of this phosphor was

# $(La_{0.65}Ce_{0.15}Tb_{0.20})_2O_3\cdot 0.90P_2O_5\cdot 0.1B_2O_3$

When excited by ultraviolet light at 254 nm, it strongly emitted green light and produced an emission spectrum with a peak in the vicinity of 545 nm. The power brightness was 100, the same as for the well-known phosphor (La<sub>0.65</sub>Ce<sub>0.15</sub>Tb<sub>0.20</sub>)PO<sub>4</sub>. However, after reheating in air at 600°C for 15 minutes, (almost the same conditions as used in the baking step), the powder brightness of the prior art phosphor decreased by 25%, while the phosphor according to the present invention decreased by but 7%.

To measure their endurance under ultraviolet light at 185 nm, both of the phosphors were irradiated for 30 minutes in a nitrogen atmosphere by a low pressure mercury vapor discharge lamp consisting of a quartz tube radiating ultraviolet light at 185 nm and 254 nm. After 30 minutes, the powder brightness of the prior art phosphor decreased by 7%, but that of the phosphor according to the 30 present invention by only 4%.

To investigate the emission output of these phosphors, they were incorporated by standard methods into 40 watt fluorescent lamps (FL40S). The output using the prior art phosphor was 4350 lumens, while the output using the present phosphor was 4750 lumens.

## EXAMPLES 2-7

35

Using the same technique as for Example 1, the boron content of the phosphor was gradually varied. The composition and characteristics of the phosphors are shown in Table 1.

TABLE 1

			% Decrease in Brightness	Brightness	
Example Number	Phosphor	Powder Brightness	After Heating	After UV Irradiation at 185 nm	Emission Output (lumens)
-	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.90P <sub>2</sub> O <sub>5</sub> · 0.10B <sub>2</sub> O <sub>3</sub>	100	7	4	4760
2	(La <sub>o.65</sub> Ce <sub>o.15</sub> Tb <sub>o.20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.95P <sub>2</sub> O <sub>5</sub> · 0.05B <sub>2</sub> O <sub>3</sub>	100	20	9	4500
က	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.80P <sub>2</sub> O <sub>5</sub> · 0.20B <sub>2</sub> O <sub>3</sub>	100	7	4	4760
4	(La <sub>0,66</sub> Ce <sub>0,15</sub> Tb <sub>0,20</sub> ) <sub>2</sub> O <sub>3</sub> · O.65P <sub>2</sub> O <sub>6</sub> · 0.35B <sub>2</sub> O <sub>3</sub>	66	16	9	4510
. 5	(La <sub>0,66</sub> Ca <sub>0,16</sub> Tb <sub>0,20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.50P <sub>2</sub> O <sub>6</sub> · 0.50B <sub>2</sub> O <sub>3</sub>	95	19	7	4430
9	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.40P <sub>2</sub> O <sub>5</sub> · 0.60B <sub>2</sub> O <sub>3</sub>	97	21	7	4410
7	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> ·0.20P <sub>2</sub> O <sub>5</sub> ·0.80B <sub>2</sub> O <sub>3</sub>	06	20	7	4310
	Comparative Example 1 (La <sub>o.as</sub> Ce <sub>o.1s</sub> Tb <sub>o.20</sub> )BO <sub>3</sub>	80	10	က	4300
	Comparative Example 2 (La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> )PO <sub>4</sub>	100	25	7	4350

The X-ray diffraction patterns of Examples 1—6 greatly resemble those of monoclinic monazites (i.e. they greatly resemble the diffraction pattern of Comparative Example 2). The X-ray diffraction pattern of Example 7 appears as an overlap of the diffraction pattern of a monoclinic monazite and of Comparative Example 1, and thus can be thought of as a mixture of the two.

From the point of view of lamp properties, when boron alone is used, the boron content per 1 gram atom of Group III B elements (i.e. the total of lanthanum, cerium, and terbium) is desirably no more than 0.6 gram atoms and preferably no more than 0.35 by no less than 0.05 gram atoms.

In the above examples, the effect of boron is not to accelerate the reaction at the time of synthesizing. Rather, boron can be thought of as displacing phosphorous in the phosphor and exerting some sort of action on the base crystal of the phosphor, based on the fact that when the phosphors of the above examples are dispersed in water, substantially no boron dissolves. Further, even if the amount of boron in the phosphor is increased to as high as 0.6 gram atoms, a very large quantity, the X-ray diffraction pattern highly resembles that produced by monoclinic monazites.

## **EXAMPLE 8**

Using the same technique as for Example 1, an oxalate precipitate containing 0.65 gram atoms of lanthanum, 0.15 grams atoms of cerium, and 0.20 gram atoms of terbium was produced. The precipitate was heated at 1000—1100°C for approximately 1 hour to obtain oxides. These oxides were thoroughly mixed with 1.00 moles of diammonium hydrogen phosphate, 0.01 moles of lithium carbonate(Li<sub>2</sub>CO<sub>3</sub>), and 0.04 moles of boric acid, then baked, pulverized, and sieved under the same conditions as for Example 1 to obtain a phosphor having the composition.

# (La<sub>0.65</sub>Ce<sub>0.15</sub>Tb<sub>0.20</sub>)<sub>2</sub>O<sub>3</sub>·P<sub>2</sub>O<sub>5</sub>·0.02Li<sub>2</sub>O<sub>3</sub>·0.04B<sub>2</sub>O<sub>3</sub>.

When excited by ultraviolet light at 254 nm, this phosphor exhibited strong emission of green light.
Figure 1 shows the emission spectrum of this phosphor. It had a powder brightness of 110, which decreased by 5% after heating in air at 600°C. Irradiation by ultraviolet light at 185 nm produced at 2% decrease in the brightness degree. The lamp emission output using this phosphor was 5150 lumens, and it has an X-ray diffraction pattern highly resembling that of monoclinic monazites. The characteristics of this phosphor are shown in Table 2.

TABLE 2

			% Decrease in Brightness	Brightness	ama j
Example Number	Phosphor	Powder Brightness	After Heating	After UV Irradiation at 185 nm	Emission Output (lumens)
8	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	110	2	2	5150
6	(La <sub>0.65</sub> Ca <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.005Ll <sub>2</sub> O · 0.01B <sub>2</sub> O <sub>3</sub>	107	4	2	5100
10	(La <sub>0.45</sub> Ca <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.04Li <sub>2</sub> O · 0.08B <sub>2</sub> O <sub>3</sub>	113	æ	က	5150
11	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.10Li <sub>2</sub> O · 0.10B <sub>2</sub> O <sub>3</sub>	110	15	4	4800
12	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.20Li <sub>2</sub> O · 0.20B <sub>2</sub> O <sub>3</sub>	101	24	7	4430
13	$(La_{0.65}Ce_{0.15}Tb_{0.20})_2O_3 \cdot 1.00P_2O_5 \cdot 0.01Li_2O \cdot 0.07B_2O_3$	113	9	2	5150
14	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.03Li <sub>2</sub> O · 0.02B <sub>2</sub> O <sub>3</sub>	110	5	2	5150
15	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.02P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	110	9	2	5150
16	(La <sub>0.45</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 0.96P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	115	7	7	5050
17	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O	105	10	2	4860

TABLE 2 (Cont'd.)

			% Decrease in Brightness	Brightness	_
Example Number	Phosphor	Powder Brightness	After Heating	After UV Irradiation at 185 nm	Emission Output (lumens)
18	{La <sub>0,65</sub> Ce <sub>0,15</sub> Tb <sub>0,20</sub> } <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Na <sub>2</sub> O	103	13	3	4700
19	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> ·1.0όP <sub>2</sub> O <sub>5</sub> ·0.02Κ <sub>2</sub> Ο	100	15	4	4620
20	$(La_{0.65}Ce_{0.15}Tb_{0.20})_2O_3 \cdot 1.00P_2O_5 \cdot 0.01Cs_2O$	66	13	4	4570
21	(La <sub>0,65</sub> Ce <sub>0,15</sub> Tb <sub>0,20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.01Rb <sub>2</sub> O	86	13	4	4540
22	(La <sub>0.65</sub> Ca <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.01Li <sub>2</sub> O · 0.01K <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	103	10	က	4800
23	(La <sub>0,65</sub> Ce <sub>0,15</sub> Tb <sub>0,20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.01CS <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	101	σ	က	4770
24	(La <sub>0.65</sub> Ca <sub>0.15</sub> Tb <sub>0.20</sub> / <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.01In <sub>2</sub> O <sub>3</sub>	100	4	9	4800
25	(La <sub>0.65</sub> Ce <sub>0.16</sub> Tb <sub>0.20</sub> l <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.03In <sub>2</sub> O <sub>3</sub>	86	က	7	4760
26	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.10In <sub>2</sub> O <sub>3</sub>	80	2	7	4430
27	(La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> / <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.01In <sub>2</sub> O <sub>3</sub> · 0.01B <sub>2</sub> O <sub>3</sub>	100	က	7	4810

## EXAMPLES 9-27

Using the same technique as for Example 8, the phosphors shown in Table 2 were prepared to determine the effects of various elements in various concentrations. Of the phosphors shown in this table, those containing an alkali metal were prepared by using a carbonate of the alkali metal as a starting material, while those containing indium were prepared by using indium nitrate trihydrate [In(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O] as a starting material.

5

Upon excitation by ultraviolet light at 254 nm, all of the phosphors in Table 2 exhibited strong emission of green light. In addition, their X-ray diffraction patterns were very similar to those of monoclinic moazites.

Comparison of the characteristics of the phosphors in Tables 1 and 2 clearly shows that the simultaneous incorporation of boron and an alkali metal produces extremely beneficial effects. The power brightness, the decrease in brightness after heating in air at 600°C, and the decrease in brightness after irradiation by ultraviolet light at 185 nm were all very satisfactory. In addition, an extremely high lamp emission output was obtained. Among the alkali metals used, lithium was 15 particularly effective in producing these desirable results.

10

As can be seen from Examples 8-12, for each gram atom of Group III B elements (the total of lanthanum, cerium, and terbium), it is desirable that the amount of alkali metal be no more than 0.2 gram atoms. Comparison of Tables 1 and 2 also shows that the desirable amount of boron is much lower for phosphors containing both boron and an alkali metal than for phosphors containing only 20 boron. As Example 9 indicates, even a boron content as low as 0.01 gram atoms produces fully satisfactory characteristics. The inclusion of indium is particularly effective in minimizing the percent decrease in brightness due to heating in air at 600°C. For each gram atom of Group III B elements (the total of lanthanum, cerium, and terbium), an indium content of no more than 0.1 gram atoms is desirable.

20

15

25 EXAMPLE 28

25

Using the same technique as for Example 1, an oxalate precipitate comprising 0.65 gram atoms of lanthanum, 0.15 gram atoms of cerium, and 0.20 gram atoms of terbium was produced. Oxides were obtained by heating the resultant oxalate at 1000-1100°C for approximately one hour. These oxides were thoroughly mixed with 1.00 mole of diammonium hydrogen phosphate and 0.025 moles of lithium fluoride (LiF). After being baked, pulverized, and sieved under the same conditions as for Example 1, a phosphor was obtained having the composition

30

# $(La_{0.65}Ce_{0.16}Tb_{0.20})_2O_3\cdot 1.00P_2O_5\cdot 0.05LiF.$

Excitation of this phosphor by ultraviolet light at 254 nm produced strong emission of green light. It has a powder brightness of 109, which decreased by 6% after heating in air at 600°C and which decreased 35 by 2% after irradiation by ultraviolet light at 185 nm. A lamp incorporating this phosphor had an emission output of 5100 lumens, and the phosphor has an X-ray diffraction pattern highly resembling that of monoclinic monazites.

35

## EXAMPLES 29-32

The same technique was employed as for Example 28, using either lithium fluoride or lanthanum 40 fluoride in various concentrations as a starting material. The contents and characteristics of the phosphors thus formed are shown in Table 3.

40

TABLE 3

			% Decrease in Brightness	Brightness	E
Example Number	Phosphor	Powder Brightness	After Heating	After UV Irradiation at 185 nm	Emission Output (lumens)
28	28 (La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.05LiF	109	9	2	5100
29	29 (La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02LiF	110	8	2	5100
30	30 (La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.05LiF · 0.02B <sub>2</sub> O <sub>3</sub>	109	4	2	5150
31	31 (La <sub>0.65</sub> Ce <sub>0.15</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.20LiF	80	0	2	4450
32	32 (La <sub>0.65</sub> Ce <sub>0.16</sub> Tb <sub>0.20</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02LaF <sub>3</sub>	100	10	2	4700

All of these phosphors have X-ray diffraction patterns greatly resembling those of monoclinic monazites. Excitation by ultraviolet light at 254 nm produced strong emission of greeen light. For each gram atom of Group III B elements (the total of lanthanum, cerlum, and terbium), a fluorine content of no more than 0.1 gram atoms is desirable.

# 5 EXAMPLES 33---43

5

Using the same technique as for Example 1, oxalates were formed containing various amounts of lanthanum, cerium, terbium, yttrium, and lutetlum. Then, using the same technique as for Example 8, a number of phosphors were obtained. The results are shown in Table 4.

TABLE 4

			% Decrease in Brightness	n Brightness	8
Example Number	Phosphor	Powder Brightness	After Heating	After UV Irradiation at 185 nm	Emission Output (lumens)
33	(La <sub>0.80</sub> Ce <sub>0.05</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	101	2	0.5	4900
34	(La <sub>0,70</sub> Ce <sub>0,15</sub> Tb <sub>0,15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	109	22	2	5100
35	(La <sub>0.55</sub> Ce <sub>0.30</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	110	ß	4	5040
36	(La <sub>0.35</sub> Ce <sub>0.50</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	111	5	7	5000
37	(La <sub>0.05</sub> Ce <sub>0.80</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	110	ß	10	4890
38	(Ce <sub>0.85</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	107	ß	14	4740
39	(La <sub>0.66</sub> Ce <sub>0.30</sub> Tb <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O-0.04B <sub>2</sub> O <sub>3</sub>	06	മ	4	4500
40	(La <sub>0.40</sub> Ce <sub>0.30</sub> Tb <sub>0.30</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	95	ß	4	4610
41	(La <sub>0.45</sub> Gd <sub>0.10</sub> Ce <sub>0.30</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>6</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	107	2	4	4950
42	(La <sub>0.45</sub> Y <sub>0.10</sub> Ce <sub>0.30</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	105	7	ហ	4810
43	(La <sub>0.50</sub> Lu <sub>0.05</sub> Ce <sub>0.30</sub> Tb <sub>0.15</sub> ) <sub>2</sub> O <sub>3</sub> · 1.00P <sub>2</sub> O <sub>5</sub> · 0.02Li <sub>2</sub> O · 0.04B <sub>2</sub> O <sub>3</sub>	107	7	2	4860

10

15

20

25

The X-ray diffraction patterns of Examples 33—43 greatly resemble those of monoclinic monazites. Excitation by ultraviolet light at 254 nm produces strong emission of green light. As the cerium content increases, the decrease in brightness due to irradiation by ultraviolet light at 185 nm also increases. For this reason, even though the powder brightness is a maximum for a relatively high cerium content, the lamp emission output is a maximum for a relatively low cerium content. For each gram atom of Group III B elements in the phosphor (the total of lanthanum, cerium, and terbium), the content of cerium is desirably no less tha 0.05 and no greter than 0.8 gram atoms. For each gram atom of Group III B elements, if the content of terbium is 0.05 to 0.3 gram atoms, a bright phosphor can be obtained.

Examples 41—43 show that it is also possible to incorporate into the phosphate the Group III 2 elements gadolinium, yttrium, and lutetium.

Now, a low pressure mercury vapor discharge lamp according to the present invention will be described. The embodiment of this lamp shown in Figure 2 is a 40 watt discharge lamp. It will be noted that the structure of this lamp is perfectly conventional. It comprises a sealed elongated light transmitting envelope 1, a pair of discharge electrodes 2 and 3 positioned at opposite ends of the envolope 1, a filling 4 comprising mercury enclosed within the envelope 1, and a phosphor layer or layers 5 coated on the inner surface of the envelope 1.

The unique feature of the present lamp is the composition of the phophor layer or layers, which comprises a phosphor according to the present invention. The following examples show the characteristics of various embodiments of this low pressure mercury vapor discharge lamps employing the phosphor according to the present invention.

## **EXAMPLE 44**

The inner surface of the glass envelope 1 of a lamp like the one shown in Figure 2 was coated with the phosphor of Example 8. The initial luminous flux of this lamp was 5150 lumens. Even after 100 hours of operation, the luminous flux decreased by only 2% to 5050 lumens. A lamp using Comparative Example 2 of Table 1, a terbium-activated lanthanum cerium orthophosphate phosphor, had an initial luminous flux of 4350 lumens, which after 100 hours of operation decrease by 5% to 4130 lumens.

## **EXAMPLE 45**

50% by weight of the phosphor of Example 8, 26% by weight of a europium-activated yttrium oxide phosphor (a red-orange-emitting phosphor having an emission peak at 611 nm), and 24% by weight of a europium-activated strontium barium chlorophosphate phosphor (a blue-emitting phosphor with an emission peak at approximately 445 nm) were mixed and then coated on the inner surface of the glass envelope 1 of a 40 watt low pressure mercury vapor discharge lamp like the one shown in Figure 2. The resulting lamp was a 3-band fluorescent lamp of high efficiency and high color rendition.

35 The color temperature of the lamp was 5000°K, the general color rendering index was 84, and it had an initial luminous flux of 3750 lumens. When Comparative Example 2 of Table 1 (a terbium-activated lanthanum cerium orthophosphate phosphor) was incorporated into the lamp as a green-emitting phosphor, there was no change in the color temperature or the general color rendering index, but the initial luminous flux was reduced to 3200 lumens. The spectral distribution of Examples 45 is shown in Figure 3.

## **EXAMPLE 46**

To obtain a 3-band fluorescent lamp of low color temperature, 45% by weight of the phosphor of example 8 and 55% by weight of a europium-activated yttrium oxide phosphor were mixed and then coated on the glass envelope 1 of a discharge lamp like the one shown in Figure 2. The resulting lamp was of high efficiency and high color rendition, with a color temperature of 2700°K. The emitted light was very similar to that of an incandescent lamp, with a general color rendering index of 87, and an initial luminous flux of 3600 lumens.

## **EXAMPLE 47**

48% by weight of the phosphor of Example 15, 25% by weight of a europium-activated yttrium
oxide phosphor, and 27% by weight of a europium-activated barium magnesium aluminate phosphor (a
blue-emitting phosphor with an emission peak at approximately 450 nm) were mixed and then coated
on the glass evelope 1 of a lamp like the one shown in Figure 2 to obtain a 3-band fluorescent lamp.
This lamp had a color temperature of 5000°K, a general color rendering index of 84, and an initial
luminous flux of 3680 lumens.

## 55 EXAMPLE 48

55
50% by weight of the phosphor of Example 36, 24% by weight of a europium-activated yttrium oxide phosphor, and 26% by weight of a europium-activated strontium calcium chlorophosphate phosphor (a blue-emitting phosphor with an emission peak at approximately 450 nm) were mixed and then coated on the glass envelope 1 of a discharge lamp like the one shown in Figure 2 to obtain a 3-60 band fluorescent lamp. This lamp had a color temperature of 5000°K, a general color rendering index of

25

35

40

45

84, and an initial liminous flux of 3679 lumens.

#### **EXAMPLE 49**

36% by weight of the phosphor of Example 29, 18% by weight of a europium-activated yttrium oxide phosphor, 18% by weight of a europium-activated strontium calcium barium chlorophosphate phosphor (a blue-emitting phosphor with an emission peak at approximately 450 nm), and 28% by weight of an antimony manganese-activated calcium halophosphate phosphor were mixed and then coated on the glass envelope 1 of a discharge lamp like the one shown in Figure 2 to obtain a 3-band fluorescent lamp. This lamp had a color temperature of 5000°K, a general color rendering index of 81, and an initial luminous flux of 3580 lumens.

10 EXAMPLE 50 10

A 3-band fluorescent lamp having a plurality of phosphate layers was fabricated. First, an antimony manganese-activated calcium halophosphate phosphor was coated on the inner surface of the glass envelope 1 of a lamp like the one shown in Figure 2. On top of this layer, a mixture containing the phosphors of Example 45 was coated. This lamp, which allows a saving in the amount of phosphor mixture used, had a color temperature of 5000°K, a general color rendering index of 83, and an initial luminous flux of 3700 lumens.

15

### **CLAIMS**

30

35

40

45

1. A phosphor having a monoclinic monazite-type crystal structure comprising:

a phosphate of the Group III B elements cerium and terbium or of cerium, terbium, and at least one 20 other element of Group III B of the Periodic Table selected from the group consisting of lanthanum, yttrium, gadolinium, and lutetium; and

at least one element selected from the alkali metals, fluorine, indium, and boron.

2. A phosphor as claimed in claim 1, wherein said phosphor contains at most 0.2 gram atoms of an alkali metal, at most 0.1 gram atoms of fluorine, at most 0.1 gram atoms of indium, and at most 0.6 25 gram atoms of boron per each gram atom of Group III B elements contained in said phosphor.

3. A phosphor as claimed in claim 1 or claim 2, wherein said phosphor contains the alkali metal lithium.

4. A phosphor as claimed in claim 1, 2, or 3, wherein the amount of cerium per gram atom of Group III B elements contained in said phosphor is at least 0.05 and at most 0.8 gram atoms.

5. A phosphor as claimed in claim 1 and substantially as set forth in any of the foregoing 30 Examples.

6. A low pressure mercury vapor discharge lamp comprising:

a sealed elongated light-transmitting envelope;

a pair of discharge electrodes positioned at opposite ends of said envelope;

a filling enclosed within said envelope comprising mercury; and

a phosphor layer coated on the inner surface of said envelope, said phosphor layer comprising a phosphor as claimed in any of claims 1 to 5.

7. A low pressure mercury vapor discharge lamp comprising:

a sealed elongate light-transmitting envelope;

a pair of discharge electrodes positioned at opposite ends of said envelope;

a filling enclosed within said envelope comprising mercury; and

one or more phosphor layers coated on the inner surface of said envelope, each of said phosphor layers comprising a red-orange-emitting phosphor and a green-emitting phosphor and optionally a blueemitting phosphor, said green-emitting phosphor being a phosphor as claimed in any of claims 1 to 5.

8. A low pressure mercury vapor discharge lamp as claimed in claim 7, wherein said red-orange

emitting phosphor is a europium-activated yttrium oxide phosphor.

9. A low pressure mercury vapor discharge lamp as claimed in claim 7 or 8, wherein said blueemitting phosphor comprises at least one phosphor selected from the group consisting of europiumactivated alkali earth metal chlorophosphate phosphors and europium-activated barium magnesium 50 aluminate phosphors.

Printed for Her Majesty's Stationery Office by the Courier Press, Learnington Spa, 1984. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.